

INFRARED STUDIES OF HYDROGEN BONDING
THE EFFECT OF POLAR SOLUTES ON THE
INFRARED SPECTRUM OF LIQUID WATER

BY
RUSSEL LESLIE MAYCOCK
B.S., University of California, 1935

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

URBANA, ILLINOIS

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor W. H. Rodebush and to Professor A. M. Buswell whose advice and direction have made this investigation possible; also to Dr. R. C. Gore and Dr. F. T. Wall for helpful criticism and interpretation of certain phases of the problem; and finally to the Rockefeller Foundation for financial support for this research.

INTRODUCTION

The study of bound water in biological materials is of great interest to both chemists and physiologists. The methods used in investigating this problem are many and varied¹, and the early results suffered greatly from the lack of an understanding of the mechanism involved in the bonding.

Correlation of the hydrogen-bond hypothesis of Latimer and Rodebush² with the spectroscopic work of Coblenz³ led Buswell⁴ to postulate that the water is bonded through the hydrogen bond. Later Wulf and Liddel⁵ showed spectroscopically that the first harmonic of the OH group disappears when hydrogen bonding is possible. This observation established infrared spectroscopy as the most direct and the most practical method for studying bound water problems.

A number of technical difficulties have been encountered in these infrared studies⁶, and the present investigation was undertaken in an effort to develop a more precise method for studying the effect of soluble polar molecules on the infrared spectrum of water.

EXPERIMENTAL

The spectrometer used is a prism type of instrument built in this laboratory in 1936.⁷ The prism is made of rock-salt and is a 60° prism 8 centimeters high by 10 centimeters on a side. The thermocouple is of the compensating type and feeds a simple photoelectric amplifier. The source is a coiled tungsten filament operated at 6 to 7 amperes at about 6 volts in an atmosphere of argon. The radiation leaves the source through a cleaved rock salt window.

The aqueous solutions studied were made up to known concentrations by dissolving weighed amounts of reagent grade solute in distilled water and diluting to a known volume. The densities of these solutions were measured on the Westphal balance.

The spectra of the aqueous solutions were determined by running films 1.59 millimeters thick against the same thickness of pure water as the blank. By this technique the normal water spectrum was cancelled out, and only the changes in the water spectrum caused by the presence of the solute were measured. However this measured difference had to be corrected to take into account the water content of 1.59 millimeters of pure water used as a blank. Since it was found that the extinction coefficient of water varies with the thickness of the water film, it became necessary to determine the spectra of several thicknesses of water in order to establish the correction.

The bulk of the work has been done in the region of the 1.96μ band of water. This band has previously been shown⁸ to undergo significant changes as the physical environment of the water is changed.

RESULTS

Spectra of liquid water were obtained from 1.3μ to 2.3μ for several thicknesses. A partial tabulation of the extinction coefficient for water in this region is shown below. The extinction coefficient is defined by the equation

$$I = I_0 \cdot 10^{-\epsilon d}$$

where I_0 is the initial intensity of the radiation at any given wavelength, I the intensity after transmission through a thickness d of water, and ϵ the extinction coefficient of water.

Thickness, d, mm.	0.13	0.33	0.53	0.72	0.92	1.12
Wavelength, μ	Extinction coefficient, cm^{-1}					
1.4	—	8.6	8.8	10.2	10.4	9.2
1.5	—	9.2	8.0	8.4	8.0	7.8
1.6	—	4.4	4.0	4.0	3.2	3.0
1.7	5.0	3.6	3.4	3.2	2.8	2.4
1.8	4.8	5.0	4.6	4.4	4.0	4.0
1.9	20.8	18.0	19.0	18.0	17.6	16.0
2.0	33.6	32.0	29.8	26.0	25.8	23.8
2.1	14.0	14.4	13.4	12.4	12.4	12.4
2.2	9.8	9.6	9.0	8.8	8.5	8.2
2.3	10.8	10.6	9.8	10.0	10.6	10.4

d, mm.	0.05	0.10	0.20	0.40	0.60	1.00	2.00
1.44 μ	15.0	15.0	14.8	14.1	13.7	11.6	9.3
1.96 μ	48.2	47.8	46.3	37.6	19.2	7.2	—

Spectra were obtained from 1.90 μ to 2.45 μ for the solutions listed below.

Group 1		Group 2		KOH	1.3 molal
NaCl	1.3 molal	NaH ₂ PO ₄	0.63 molal		
	6.0	Na ₂ HPO ₄	0.58	Group 4	
NaBr	4.0	Na ₃ PO ₄	0.58	MeOH	1.3
LiNO ₃	4.0	NaHCO ₃	1.3	EtOH	1.3
	7.2	NaHSO ₄	1.3	Urea	1.3
NaNO ₃	4.0	NH ₄ Cl		Diethyl	
LiCl	4.0	NH ₄ I	1.3	amine	1.3
	8.0	NH ₄ OH	1.3	Trimethyl	
	9.5			amine	1.3
CaCl ₂	4.6 molal	Group 3		Acetic acid	1.3
CdCl ₂	4.0	HCl	1.3		

These spectra were corrected for water content, and the change in the extinction coefficient of the water in the solution was plotted against wavelength throughout the region studied.

DISCUSSION

The spectra of the solutions of the salts in group 1 have in common a peak of rather high positive $\Delta\epsilon$ at about $2.4\ \mu$ and a trough of negative $\Delta\epsilon$ at about $2.0\ \mu$ with an additional small peak at about $2.2\ \mu$. The solutions in group 2 are hydrolyzed to a greater or less extent and give rise to spectra in which the peak at $2.4\ \mu$ does not appear and the trough at $2.0\ \mu$ is much less pronounced. The peak at $2.2\ \mu$, however, is quite prominent and dominates the spectra in this region. The spectra of the solutions of the polar molecules in group 4 resembles in general those of group 2. However, the peak at $2.2\ \mu$ contains an undetermined contribution from the carbon-hydrogen peak at $2.3\ \mu$ in the case of all the group 4 solutions except that of urea, so that little theoretical significance can be attached to these spectra.

The three distinctive features of the spectra can be correlated with three possible effects of the solute upon the structure of the solvent water. The polar atmosphere surrounding each water molecule influences the orientation of the molecule as it takes up the highly specific position with respect to its nearest neighbors that it is necessary for association.⁹ The introduction of polar molecules of solute into this atmosphere changes the Debye field and so influences the forces involved in the association of the water. This effect would be most pronounced for high concentrations of ions. The trough at $2.0\ \mu$ shows the greatest variation with change of the concentration of ions in the solution and so can be correlated with this Debye effect.

The peak at $2.4\ \mu$ increases somewhat with increase in ionic concentration but it is also present in the spectra of the solutions in group 4 and in that of cadmium chloride, a very weak electrolyte, so that it may be correlated with a combin-

ation of the above mentioned Debye effect and the purely steric effect of their introduction of foreign molecules in the regular packing of liquid water.

The peak at 2.2μ is of the greatest interest and can be explained on the basis of hydrogen bonding between the normal water molecule and a water molecule which is in peculiar circumstances. It is recognized that the frequency of a hydrogen atom vibrating against an oxygen depends mostly upon the strength of the hydrogen-oxygen bond and to only a slight extent upon the other group to which the oxygen is bound. If a water molecule were to become bound to an ion by hydration forces, subsequent hydrogen bonding of that water molecule to a normal water molecule would result in a hydrogen bond of abnormal bond strength. In the same manner hydrogen bonding of either a hydroxonium ion, HOHOH^- , or a hydronium ion H_2OH^+ would produce an abnormal bond. If we can assume that in such cases the hydrogen bond so formed is of about the same strength, then all such abnormal hydrogen bonds should result in an absorption peak at about the same wavelength. It is easily seen that the peak at 2.2μ fulfills all the requirements for such an absorption peak. In the simple salts in group 1 hydration of the ions can occur to some extent, but here the amount of hydronium or hydroxonium ion is very small and the peak at 2.2μ is relatively small. Furthermore calcium chloride which is more highly hydrated than the other salts listed, shows a higher 2.2μ peak. The salts in group 2 undergo considerable hydrolysis in solution so that either hydronium or hydroxonium is present. These salts show very high 2.2μ peaks. The peak is quite high for Na_3PO_4 , which is quite alkaline in solution, and much smaller for Na_2HPO_4 , which is only slightly alkaline, and for NaH_2PO_4 , which is slightly acid. The practically neutral NaHCO_3 shows a very small 2.2μ peak, while Na_2CO_3 , which is alkaline shows a peak comparable in height to Na_3PO_4 of about half the concentration. The ammonium salts which are acid show high 2.2μ peaks as does also NH_4OH . Both KOH and HCl give high

2.2 μ peaks and no other structure in this region. This is good confirmation of the original assumption that the hydroxonium ion and the hydronium ion form hydrogen bonds of about the same strength.

BIBLIOGRAPHY

1. Fisher, H., Thesis: Doctor of Philosophy, U. of Illinois (1936).
2. Latimer and Rodebush, J. Am. Chem. Soc., **42**, 1419 (1920).
3. Coblenz, J. Frank. Inst., **172**, 309 (1911).
4. Buswell, Am. Chem. Soc. Mon., **38**, 53, 60 (1928).
5. Wulf, Liddel and Hendricks, J. Am. Chem. Soc., **57**, 1464 (1933).
6. Bernal and Fowler, J. Chem. Phys., **1**, 515 (1933); Downing, J. R., Thesis: Doctor of Philosophy, U. of Illinois (1940).
7. Claussen, W. F., Thesis: Doctor of Philosophy, U. of Illinois (1939).
8. Collins, Phys. Rev., (2), **20**, 486 (1922); **26**, 771 (1925); Plyler, J. Opt. Soc. Amer., **9**, 545 (1924); Ganz, Ann. d. Physik, (5), **28**, 445 (1937); Suhrmann and Breyer, Z. physik. Chem., **B20**, 17 (1933).
9. Piekara, Acta Phys. Polon., **6**, 130 (1937).

VITA

Russel Leslie Maycock was born in Springville, Utah on October 13, 1912. He attended grammar school in Springville, Utah and San Francisco, California. From 1927 to 1931 he attended Mission High School in San Francisco. He was awarded a California Scaife Scottish Rite Scholarship and spent the year 1931-1932 at the California Institute of Technology and the years 1932-1935 at the University of California at Berkeley. After receiving the degree of Bachelor of Science with Honors in 1935, he worked at industrial chemical research for the Shell Development Company at Emeryville, California for three years. In 1938 he was granted a Special Research Assistantship in physical chemistry made possible through the Rockefeller Foundation and entered the Graduate School of the University of Illinois. He was married to Miss Elizabeth L. Weston in December, 1940. He is a member of Sigma Xi and Phi Lambda Upsilon.



Digitized by the Internet Archive
in 2026

